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Mechanical and Thermal Properties of LENR Modified Epoxy Composite

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ABSTRACT

Epoxy resins are considered as one of the most important classes of thermosetting polymers for many industrial applications and become an important matrix in polymer composites. However polymerization of this resin resulted in brittleness due to high crosslinking level. Due to this matter, many efforts have been made to improve the toughness of cured epoxy resins by the introduction of rigid particles, reactive rubbers, interpenetrating polymer networks and thermoplastics within the matrix. Incorporation of small amount of rubber is one of the approaches to improve fracture toughness of the epoxy matrix. In this work, the flexural and impact properties of liquid epoxidized natural rubber (LENR) modified epoxy composites have been studied. Addition of LENR increased the impact strength of the epoxy resin. The impact strength increased from to 18.357 kJ/m², when modified with 5.5 phr LENR. The SEM analysis shows uniform dispersion of rubber particles within the epoxy matrix with average particle size less than 1 μm.

Keywords: *Epoxy resin, modified epoxy, liquid epoxidized natural rubber (LENR), impact strength, toughened epoxy*

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Introduction

Epoxy resins are a large family of resins that represent some of the high performance resins available in the market. Epoxies are generally out perform most other resin types in terms of mechanical properties and resistance to environmental degradation, which leads to their almost exclusive use in the aircraft industry. As a laminating resin their increased adhesive properties and resistance to water degradation make these resins ideal for use in applications such as boat building. Here epoxies are widely used as a primary construction material for high performance boats or as a secondary application to sheath a hull or replace water degraded polyester resins and gel coats [1].

Epoxy resins are characterized by the presence of a three membered ring known as the epoxy, epoxide, oxirane or ethoxyline group. Commercial epoxy resins contain aliphatic, cycloaliphatic or aromatic backbones. The most widely used one is epichlorohydrin and bisphenol-A derived resins. These epoxy resins are considered as one of the most important classes of thermosetting polymers and are extensively used for their many good properties which include high stiffness and strength, creep resistance, chemical resistance and good adhesion to many substrates [2].

They are characterized by high chemical and corrosion resistance as well as good mechanical and thermal properties once cured. However, in many applications they have disadvantage of brittleness with poor resistance to crack propagation and low impact strength and therefore, exhibit low toughness. Many researches have been worked out to increase the toughness such as by using glass beeds, alumina trihydrate and silica. The most successful works involving the addition of a suitable rubber such as liquid amine-terminated (ATBN) [2], carboxyl-terminated (CTBN) [3-6], hydroxyl-terminated (HTBN) [7-9], epoxy-terminated (ETBN) copolymers of butadiene and acrylonitrile [10], hydroxyl-terminated and epoxy-terminated polybutadiene to interpenetrating the polymer networks (IPN) structures [2]. Another method is by addition of suitable rubbers that are copolymers with variable acrylonitrile contents to the uncured epoxy resins. The effects of the acrylonitrile content of the copolymer type, the molecular weight, the concentration, and the solubility parameter of the rubber and its functional end groups, on the fracture toughness and impact strength have been studied.

It has been reported that modification of epoxy resins by addition of rigid particle, which leads to a significant reduction in cost and a considerable improvement in the resin's mechanical, thermal and electrical properties. Parameters such as the volume fraction of the filler, particle size, modulus and strength of the filler, resin-filler adhesion and toughness of the matrix have been extensively studied. The variation of these parameters leads to improve toughness of these resins while increasing its strength and modulus [2, 13].

In this research, liquid epoxidized natural rubber was used with the epoxy resin as the matrix. With the photochemical degradation technique, the long chains of the epoxidized natural rubber turn to be the shorter one with a lower molecular weight.

Experimental Details

Materials

The materials used in this study were epoxy and hardener (Morcote BJC 39) supplied by Vistec Technology Sdn Bhd whereas the epoxidized natural rubber (ENR-50) was supplied by Malaysian Rubber Board. Liquid epoxidized natural rubber (LENR) was prepared using photochemical degradation technique in the UKM laboratory [11].

Liquid Epoxidized Natural Rubber (LENR) Preparation

Epoxidized natural rubber (ENR-50) was cut into small pieces for mastication process. Then, the ENR was soaked in toluene together with rose Bengal, methylene blue and methanol. The process was done for 24 hours. Then, the natural rubber was slowly stirred with addition of toluene to aid the stirring process and to well mix the natural rubbers. The stirred process was kept until the colour change for approximately 7 to 10 days under the exposure of white light. Good LENR exhibit pale yellow colour and sticky.

Composite Preparation

Epoxy-LENR composites were fabricated in the form of plate using a stainless steel mould measuring 165 × 165 × 3 mm. Epoxy resins was mixed with epoxidized natural rubber at different rubber concentration (1.5 to 7.5 phr) and stirred for 1 hour. Stoichiometric amount of hardener was added to the mixture and stirred for 1 minute. Then, the mixture was poured into the mould. The mould was then placed between the heated platens of a hot press under 8 MPa pressure at 100°C for 25-30 minutes. The plates were cut into sizes according to the testing types using diamond blade cutter. For mechanical testing, 10 specimens were tested for each batch to get the average values.

Test Methods

Flexural Test

The flexural strength and flexural modulus was determined according to ASTM D790-96. A gauge length of 100 mm was employed with a cross-head speed

of 5 mm/min using Shimadzu Universal Testing Machine (model: Autograph AG-X 50kN).

Izod Impact Test

The impact strength is determined using Ray Ran Pendulum Impact System according to ASTM D256-88.

FTIR (Infrared Spectroscopy)

FTIR Spectroscopy was used to monitor the extent of chemical reactions of the epoxy resin-LENR systems. The samples were analysed by Fourier transform infrared spectroscopy. For the infrared studies, a small portion of the epoxy-LENR system was attrition on potassium bromide (KBr) pellet.

TGA

Thermal degradation studies of the composite were performed using Metler Toledo STGA851 thermogravimetric analyzer with a heating rate of 10°C/min with nitrogen gas flow from room temperature to 650°C.

Morphologycal Examination

Fractured surfaces of samples of epoxy resins modified ENR with different phr of LENR were coated with a thin gold layer and examined using a scanning electron microscope (Philips XL 30).

Results and Discussion

Flexural Properties of Modified Epoxy Composite

Figure 1 and Figure 2 depicts the flexural properties of neat and rubber modified epoxy resin composites. The flexural strength and modulus of the modified samples are lower than that of unmodified epoxy. The phase separated created by rubber domains impart reduction in modulus. A very small amount of rubber may get incorporated into the epoxy matrix; thereby it gives flexibleness to the thermoset network. The rubber that is incorporated into the epoxy matrix is responsible for the reduction in flexural strength of the modified samples. Report by Ozturk et al., on their work on rubber modified epoxies support this observation [8].

Similar observation is reported by M. Abadyan et al. regarding the decrease in flexural properties with increase of rubber content [12]. Rubber modifiers are

generally known to affect mechanical properties depending on their compatibility with the matrix, particle size, shape and content as well as the intrinsic strength of the rubbery phase.

Figure 1 shows the flexural modulus of epoxy resin as a function of rubber content. As expected the flexural modulus gradually decreases with increasing rubber content. This is due to the fact that the strength and modulus of rubber is much lower than that of epoxy matrix. In addition, low modulus rubber particles act as a stress concentrators and decrease the yield strength. Reduction of the macroscopic yield stress leads to promote the crack tip blunting and produce larger plastic zone around the crack tip which contributes to fracture toughness improvement [5, 8, 12].

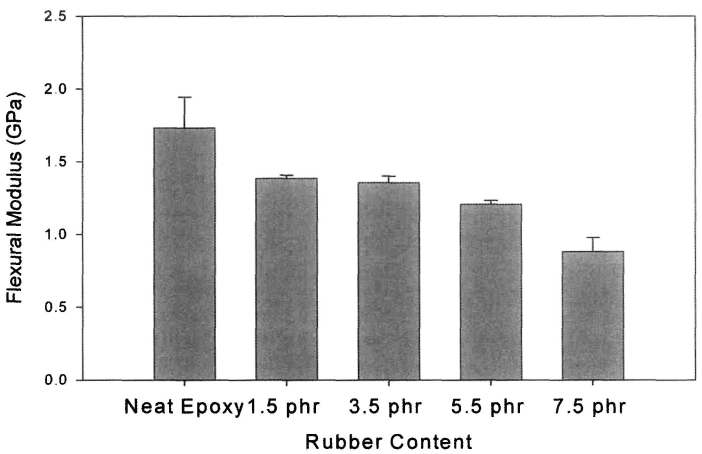

Figure 1: Flexural Modulus for Modified Epoxy Composite at Various Rubber Content

The result of flexural strength of modified epoxy was shown in the Figure 2. As seen, flexural strength of the samples gradually decrease with increasing rubber content similar to that of flexural modulus. These can be attributed to (i) weakening effect of rubber modifiers in the matrix and (ii) increase in void content due to effect of increasing viscosity of rubbery phase [5, 8, 12].

Impact Strength of Modified Epoxy Composite

Figure 3 shows the impact strength of LENR modified epoxy at varies rubber content. Impact strength increases as the rubber content increases. The impact strength of epoxy resins modified with 5.5 phr LENR was 8.26 kJ/m^2 compared to the neat epoxy which is 4.91 kJ/m^2. The improvement was 68%.

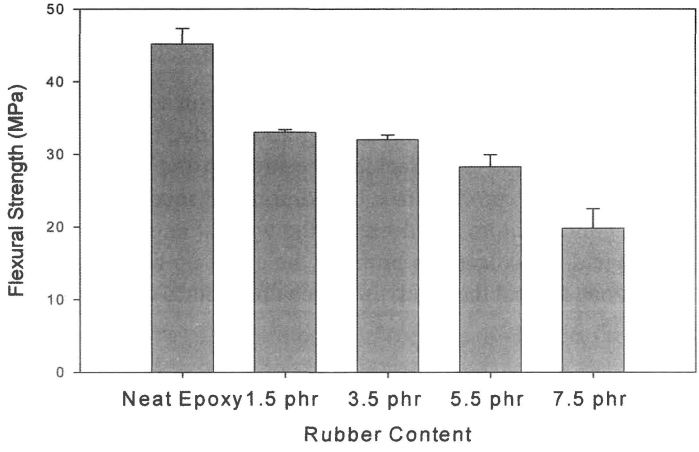

Figure 2: Flexural Strength for Modified Epoxy Composite at Various Rubber Content

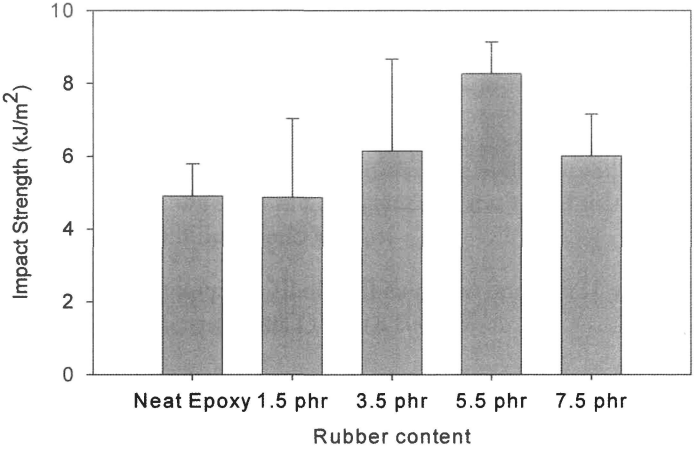

Figure 3: Impact Strength Versus Rubber Content of LENR Blends

The addition of rubber imparts an increase in the value of impact strength up to an optimum rubber content of 5.5 phr. No further increase was found on further loading of rubber. This may be attributed to the bigger size of rubber particles at higher concentrations. As seen from SEM micrographs in Figure 7, there is an increase in the size of rubber particles for 7.5 phr LENR blends. The increase in value up to an optimum level of rubber concentration attributed to the effective stress concentration behavior of the phase separated rubber-rich particles that amplify plastic deformation of a highly brittle matrix to a

certain extent. Comparatively lower performance of the present rubber at lower concentrations shall be attributed to lesser compatibility with the epoxy resin [8]. Similar behavior has been also reported in other rubber modified epoxy systems [14, 15].

Infrared Spectroscopy Characterization

Series of FTIR spectra have been obtained to confirm the occurrence of any chemical interaction between epoxy resin matrix and liquid epoxidized natural rubber. Figure 4 shows the FTIR spectrum of cured epoxy and epoxy/LENR. The absorption band at 1736 cm^{-1} indicates the presence of C=O groups which is derived to be an active functional groups that took part in the reaction.

From the Figure 4, it was observed that no new peak on FTIR spectrum of LENR modified epoxy. The absorption band of 1736 cm^{-1} still exist for all products. This indicates that no chemical bonding was formed between rubber particle and epoxy resin after curing.

Thermogravimetric Study

Thermal stability and thermal degradation behavior of the modified samples are derived from TGA traces which are shown in Figure 5 while Table 1 depicts the thermal degradation temperature obtained from TG curves. The onset temperature of 5% and 10% weight loss deviation from the baseline of the TG curve was used as indicator of the composite thermal stability.

The temperatures at 5% and 10% weight loss of the samples are tabulated in Table 1. It can be seen that increasing in the content of LENR resulted in decreasing in degradation temperature. A higher value of initial decomposition temperature of the neat system can probably be attributed to the higher cross linking density of the system. Inclusion of LENR creates domain of rubber particles in between the cross links which ultimately reduce the cross linking density. It is reported by Raju et al. that higher cross linking density of the neat epoxy needs more activation energy for degradation and higher temperature compared to modified epoxy [8].

Morphological Examination

From the micrographs of the fractured surface of the LENR modified epoxy composites, the results show the dependence of the microstructure on the rubber content. At the lower rubber content, the rubber particles are well dispersed in the epoxy matrix with the average particle size less than 1 μm. At higher rubber content, the rubber particles are bigger, forming agglomerations which lead to phase inversion and flexibilization of the matrix.

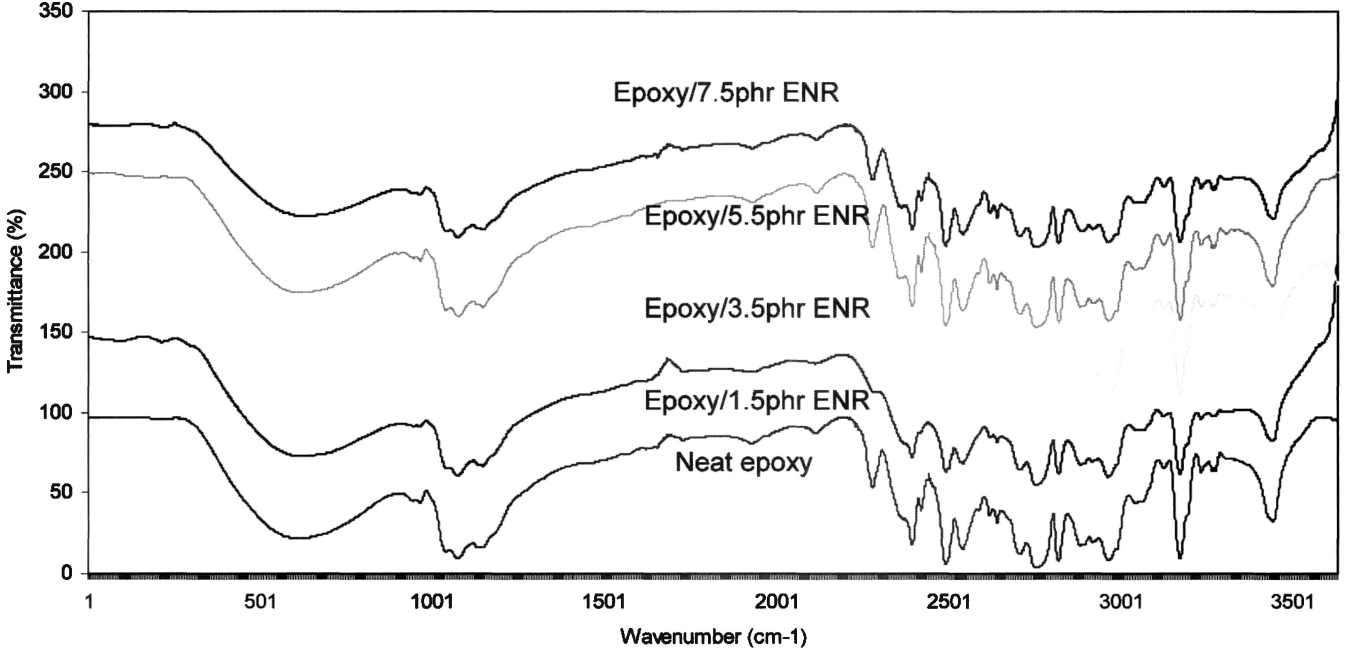

Figure 4: FTIR Spectra of the Epoxy and LENR Modified Epoxy Products

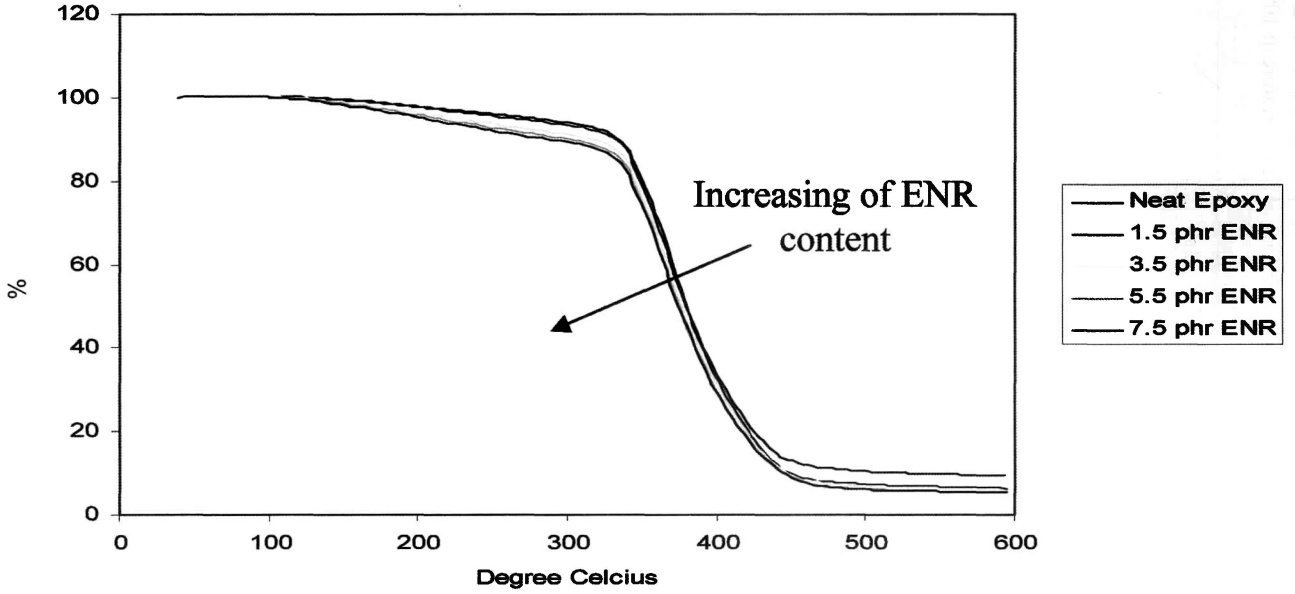

Figure 5: Thermograms of Epoxy and LENR Modified Epoxy Products

Table 1: Temperatures of Weight Loss of Neat Epoxy and LENR Modified Epoxy Samples

Samples	Temperature at 5% wt loss (°C)	Temperature at 10% wt loss (°C)
Neat epoxy	296	340
Epoxy/1.5phr LENR	270	338
Epoxy/3.5phr LENR	244	320
Epoxy/5.5phr LENR	212	296
Epoxy/7.5phr LENR	184	286

Figure 6 shows typical fractured surface of neat epoxy samples. Although there are some shear deformation lines, the relative smoothness of these fracture surfaces indicate that no significant plastic deformation has occurred.

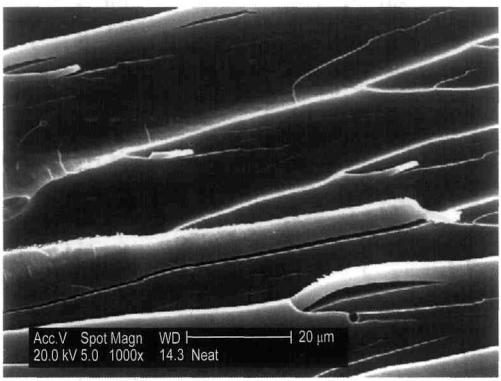

Figure 6: Relatively Smooth Fracture Surface of Neat Epoxy Samples at Magnification of 1000x

Figure 7(a) is the micrograph of 1.5 phr LENR-epoxy blend samples. This micrograph shows that rubber particles formed domains in the epoxy resins matrix. The domains were uniformly distributed through the matrix and a narrow particle size distribution was observed when the whole fracture surface was examined. Small amount of deformation lines and the smooth surfaces indicates that these samples fractured in a brittle manner.

The micrographs in Figure 7(b), (c) and (d) also show formation of rubber domains. The bright interfacial layer around the rubber domains may indicate the weak interaction between rubber particles and epoxy matrix. The mechanical test results also proved that due to this weak interaction, the flexural properties were comparably low. Relatively large amounts of deformation lines in these

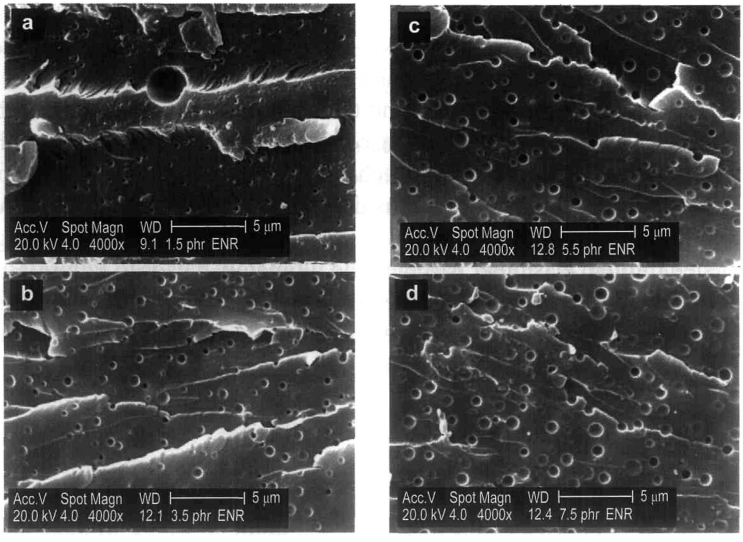

Figure 7: Rubber Domains Found in the Epoxy Matrix in (a) 1.5 phr LENR Samples, (b) 3.5 phr LENR Samples, (c) 5.5 phr LENR Samples and (d) 7.5 phr LENR Samples (at the Same Magnification of 4000 x)

micrographs indicate that the crack growth rate in these samples is reduced. The fractured surfaces are not very smooth compared to Figure 7(a). It has been reported that the size of stress whitened zone or the amount of deformation lines are proportional to the increase in toughness of the material [7].

From the micrograph in Figure 7, the calculation of the sizes of rubber domain shows that the use of 1.5 phr, 3.5 phr, 5.5 phr and 7.5 phr LENR give the average size of rubber domain 0.308 µm, 0.478 µm, 0.630 µm and 0.797 µm respectively. Number and area average domain diameters are found to increase with respect to rubber content, which is in agreement with the behavior of other rubber modified epoxy [8].

Conclusion

The mechanical performance of neat epoxy changes with the inclusion of varying phr of LENR, which is explained by the evolution of morphological changes in this LENR-epoxy blends system. The elastomeric nature of the rubber caused reduction in flexural strength and modulus but impact strength values increased and attained a maximum for 5.5 phr rubber inclusion. Some amounts of added rubbers goes into the epoxy matrix and increase the flexibility of the brittle thermoset matrix. This effect is responsible for the shear deformation

of the matrix, and thus for the prevailing toughening effect. Maximum impact strength was observed for 5.5 phr LENR-epoxy blend attributed to the presence of uniformly distributed rubber particles.

The flexural properties were found to decrease by the inclusion of rubber. The size of elastomer domains increased with the inclusion of greater phr of rubber. The poor performances of mechanical properties of modified epoxies containing 7.5 phr of rubber are considered as due to large particle size. In the modified epoxies that having lower content of elastomer, crack energy is propagated through elastomer particles and ultimately bleads to failure. But, in a higher content of elastomer modified epoxies, elastomer pull out directs the energy transfer through the interface which leads to interfacial separation and finally failure of the matrix [8].

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